# Monomeric and Octameric Divalent Ytterbium Complexes of Diphenylmethyl Dipyrrolyl Dianion

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*Summary: Dipyrrolide dianion $[Ph_2C(C_4H_3N)_2]^{2-}$ readily reacts with $YbCl_3(THF)_3$ to form a trivalent precursor, which was further reduced by using either lithium or sodium. The result of the reaction was determined by the nature of the alkali metal since octameric anionic clusters and neutral monomeric complexes were isolated in the two cases.*



## Introduction

The unique versatility of the cyclopentadienyl-based ligand system has been a significant factor in contributing to the spectacular development experienced by lanthanide chemistry in the early 1980s. However, despite the caliber of transformations discovered for low-valent lanthanide complexes during the last two decades,[1] information concerning the chemical reactivity of low-valent species supported by different ligand systems remains relatively scarce and fragmentary.[2] Recently, we have been investigating the chemistry of low-valent samarium supported by diphenylmethyl dipyrrole[3] dianions which bear some electronic and steric resemblance to bent-metallocene-type ligands. However, the presence of a hard nitrogen donor atom in the five-membered rings renders these anions more versatile for assembling polynuclear structures via formation of additional M−N $\sigma$-bonds. Given that a low-valent lanthanide atom may perform only one-electron redox reactions, the presence of two or more metal centers in the same molecular frame may be desirable for performing molecular activation processes through cooperative attack on the same substrate when availability of several electrons is required. A preliminary reactivity study carried out with this particular ligand system has so far revealed a promising feature in the chemistry of divalent samarium, having shown the ability of this ligand to assemble tetranuclear clusters able to carry out four-electron reduction of dinitrogen.[4] Thus, in an attempt to better understand the chemistry of this particular ligand system and its ability to both assemble polynuclear structures and tune the redox properties of low-valent lanthanide complexes, the less reducing and NMR accessible $Yb^{2+}$ ion was chosen for this study. In this paper, we describe the preparation of an unprecedented octameric cluster and monomeric complex of divalent Yb of the diphenylmethyl dipyrrolyl dianion obtained via reduction of an $Yb^{3+}$ precursor.

## Result and Discussion

Treatment of a solution of the lithium salt of the diphenyl dipyrromethanyl dianion with $YbCl_3(THF)_3$ followed by reduction with metallic lithium afforded dark-red crystals of $\{[Ph_2C(C_4H_3N)_2Yb]_8(\mu^3\text{-}Cl)_2\}\{Li(THF)_4\}_2 \cdot 10THF$ (**1**), which were isolated in 61% yield (Figure 1). The connectivity of **1**, which was elucidated by an X-ray crystal structure, showed a dianionic cluster formed by eight $[Ph_2C(C_4H_3N)_2Yb]$ units with the eight metal atoms arranged to form a large macrocyclic structure. The two negative charges of the octameric cluster are balanced by two identical cations located in the interstitial space and unconnected to the cluster. Both cations consist of two lithium atoms, each solvated by four molecules of THF. Similar to the tetranuclear samarium dinitrogen cluster of the same ligand system,[4] each set of adjacent ytterbium atoms is bridged by one dipyrrolide dianion, with the pyrrole rings being in turn $\pi$-bonded to one ytterbium and $\sigma$-bonded to a second. As a result, each ytterbium atom is in an ytterbocene-like environment defined by two $\pi$-bonded pyrrolyl rings from two ligands. Two chlorides reside within the framework of eight Yb atoms each bridging a set of three Yb atoms located at opposite ends of the cavity such that two ytterbium atoms remain uncoordinated to a chloride.

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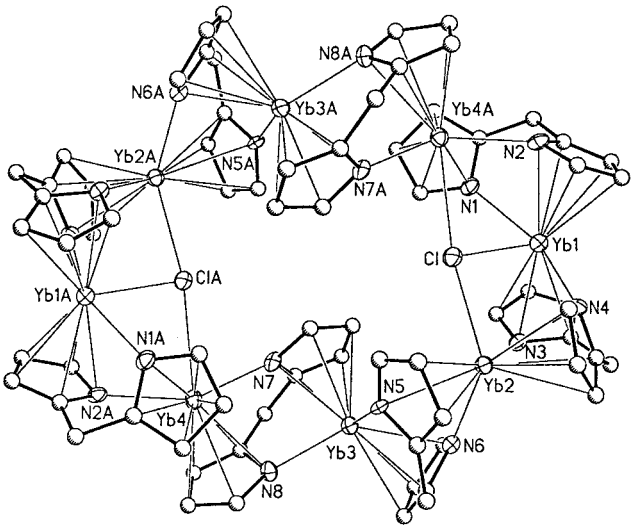


**Figure 1.** Thermal ellipsoid plot of **1**. Thermal ellipsoids are drawn at the 30% probability level. Phenyl groups were omitted for clarity.

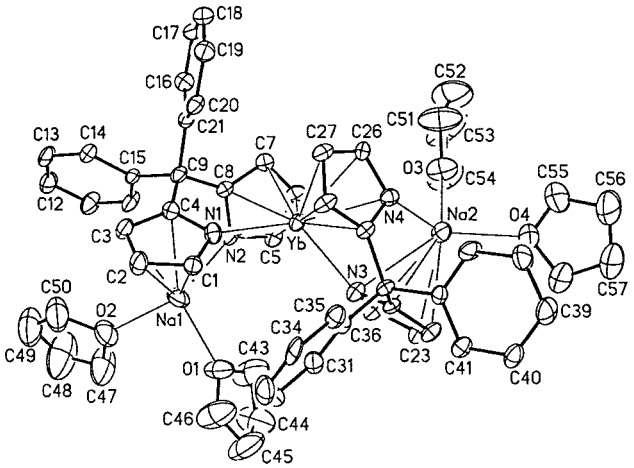


**Figure 2.** Thermal ellipsoid plot of **2**. Thermal ellipsoids are drawn at the 30% probability level.

Complex **1** is a divalent ytterbium species and is diamagnetic in the solid state. Unfortunately, the insolubility of this ionic compound in the most common organic solvents prevented NMR characterization. Finally, the octameric frame of complex **1** appears to be rather robust, and no reactivity was observed during attempts to replace the halogen atoms with more reactive functions such as hydride and alkyls.

The fact that complex **1** is the result of the *formal* addition of two LiCl units to an octameric cluster prompted us to attempt similar reaction by using sodium instead of lithium. The reduction reaction using finely dispersed metallic sodium was carried out in THF under Ar and afforded dark-red crystals of the monomeric $\{[Ph_2C(C_4H_3N)_2]Na(THF)_2\}_2Yb$ (**2**) in 75% yield (Figure 2). The monomeric nature of **2** was elucidated by an X-ray crystal structure. The complex consists of a single ytterbium atom $\pi$-bonded to two pyrrole rings of two ligands assuming an overall bent-ytterbocene arrangement very similar to that observed in complex **1**. The second pyrrole ring of each ligand is both $\sigma$-bonded to ytterbium and engaged in $\pi$-coordination with one of the sodium atoms, which are, in turn, coordinated to two molecules of THF. The coordination sphere of each sodium atom is completed by the nitrogen atom of one of the two pyrrole rings $\pi$-bonded to the ytterbium atom.

Complex **2** is diamagnetic. The $^1$H NMR spectrum is characterized by three poorly solved bands for the three nonequivalent protons of the pyrrolyl ring, while the phenyl groups display two sharp multiplets and one poorly resolved band. The simplicity of the NMR spectra, showing only one set of pyrrole and phenyl rings despite the variety of interactions with sodium and ytterbium observed in the solid-state structure, may be taken as an indication of fluxional behavior. However, spectra recorded at −60 °C were basically unchanged except for a small yet significant broadening of the spectral lines.

The structural arrangement of the ligand in complex **2** around the Yb and Na atoms is almost identical to that observed in **1.** The difference arises from the fact that the Yb atom in **2** bears two molecules of ligand. However, *regardless of the stoichiometry employed*, **2** is the only species isolated, and we found no evidence so far for the formation of higher nuclearity compounds. As well, NMR spectra of the residues from the dried mother liquors did not indicate the presence of other species. This implies that, if the ligand is exclusively used for the formation of **2**, another ytterbium compound should necessarily be present. Unfortunately, attempts to analyze the composition of the small amount of insoluble residue obtained from the reduction were unsuccessful. A stoichiometry ratio of two ligands per one ytterbium atom optimized the reaction yield to 75% of isolated crystalline material.

The apparent role of the alkali metal in determining the result of the reaction is surprising and is exclusively determined by the nature of the alkali cation. Furthermore, the fact that the ytterbium atom in **2** retains two ligands even when reactions were carried out in a 1:1 stoichiometric ratio (although yields are significantly lower in this case) indicates that (1) the dipyrrolyl ligand cannot act as a regular mononucleating chelating ligand but works instead as a bi- or polynucleating ligand and (2) the formation of a metallocenic-type structure around the lanthanide may be achieved with only two pyrrolyl rings from two ligands and is a driving force for determining the stoichiometry and the overall result of the reaction.

## Experimental Section

All operations were performed under an inert atmosphere of a nitrogen-filled drybox or by using standard Schlenk-type glassware in combination with a nitrogen-vacuum line. Solvents were dried by passing through a column of $Al_2O_3$ under an inert atmosphere prior to use, degassed in vacuo, and transferred and stored under inert atmosphere. $Ph_2C(C_4H_3NH)_2$[3] and $YbCl_3(THF)_3$[5] were prepared according to literature procedures. THF-$d_8$ was dried over Na/K alloy, vacuum-transferred into ampules, and stored under nitrogen prior to use. NMR spectra were recorded on a Bruker AMX-500 spectrometer using vacuum-sealed NMR tubes prepared inside a drybox. Infrared spectra were recorded on a Mattson 3000 FTIR instrument from Nujol mulls prepared inside the drybox. Elemental analyses were carried out using a Perkin-Elmer Series II CHN/O 2400 analyzer.

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**Preparation of {[$Ph_2C(C_4H_3N)_2$]Yb]$_8$($\mu^3$-Cl)$_2$}{Li(THF)$_4$}$_2$·10THF (1).** A solution of MeLi (15.0 mL, 1.4 M, 20.8 mmol) in diethyl ether was added at room temperature to a solution of diphenyldipyrromethane (3.1 g, 10.4 mmol) in THF (150 mL) under Ar. After stirring for 15 min, $YbCl_3(THF)_3$ (5.2 g, 10.4 mmol) was added, and the resulting suspension was stirred for 24 h at room temperature, during which time the color changed to yellow-orange. The suspension was subsequently treated with excess metallic lithium (0.1 g, 14.4 mmol). Within minutes the color began to deepen to red. Stirring proceeded for 16 h, resulting in a dark-red solution. The mixture was heated gently to dissolve the red microcrystalline solid that had accumulated, and a filtration of the hot mixture was carried out to separate unreacted lithium. The solution was concentrated to 100 mL and layered with hexanes (15 mL). After 48 h at room temperature, dark-red blocks of **1** separated (4.0 g, 0.8 mmol, 61%). IR (Nujol mull, cm$^{-1}$): 3051(w), 1597(w), 1491(m), 1462(s), 1415(m), 1377(s), 1261(m), 1232(w), 1182(w), 1155(s), 1078(m, br), 1038(s), 980(w), 964(w), 918(w), 892(m), 850(m), 800(w), 762(s), 742(s), 702(s), 659(w), 637(m). Anal. Calcd (Found) for $C_{240}H_{272}N_{16}Yb_8O_{18}Cl_2Li_2$: C 56.10 (55.92), H 5.34 (5.39), N 4.36 (4.32). Very low solubility in solvents including THF and pyridine precluded NMR characterization.

**Preparation of {[$Ph_2C(C_4H_3N)_2$]Na (THF)$_2$}$_2$Yb (2).** A solution of diphenyldipyrromethane (4.0 g, 13.4 mmol) in anhydrous THF (100 mL) was treated with NaH (0.6 g, 26.8 mmol), resulting in effervescence. Stirring proceeded for 1 h, after which time $YbCl_3(THF)_3$ (3.3 g, 6.7 mmol) was added. The resulting pale yellow suspension was stirred for 16 h. After filtration to remove a small amount of insoluble material and subsequent addition of finely dispersed, metallic sodium (0.15 g, 6.7 mmol), a vigorous stirring produced a color change to red after 5 min. After 16 h, the suspension was filtered and the deep-red filtrate was concentrated to 25 mL. Layering with hexanes (25 mL) and standing at room temperature for 2 days resulted in the separation of dark-red plates of **2** (5.5 g, 5.0 mmol, 75%). IR (Nujol mull, cm$^{-1}$): 3095(w), 3057(w), 2727(w), 2684(w), 1597(m), 1491(s), 1462(vs), 1443(s), 1417(m), 1377(m), 1261(w), 1233(w), 1178(w), 1153(w), 1095(w), 1049(vs), 978(w), 918(w), 893(m), 850(m), 841(w), 798(w), 766(s), 746(vs), 730(vs), 706(vs), 658(m), 636(s). Anal. Calcd (Found) for $C_{58}H_{64}O_4N_4Na_2Yb$: C 63.32 (63.16), H 5.86 (5.82), N 5.09 (5.07). $^1$H NMR (THF-$d_8$, 500 MHz, 60 °C): $\delta$ 10.00 (br s, 1H, pyrrolyl), 7.16 (m, 2H, phenyl), 6.93 (m, 2H, phenyl), 6.68 (br s, 1H, phenyl), 5.89 (s, 1H, pyrrolyl), 5.71 (br s, 1H, pyrrolyl), 3.58 (br s, THF), 1.73 (br s, THF). $^{13}$C NMR (THF-$d_8$, 125.72 MHz, 23 °C): $\delta$ 127.35, 104.57 (C−H pyrrolyl), 128.70, 127.35, 125.60 (C−H phenyl), 68.21 (THF coord), 26.37 (THF coord), 149.90, 131.33, 60.02 (quaternary C).

**X-ray Crystallography.** Suitable crystals were selected, mounted on thin, glass fibers using paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° $\omega$-scans at 0°, 90°, and 180° in $\phi$. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[6]

Systematic absences in the diffraction data and unit-cell parameters were uniquely consistent with the reported space group. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on $F^2$. All non-hydrogen atoms were refined with anisotropic displacement parameters for complex **2**. In the case of **1** all non-hydrogen atoms were located. However only the ytterbium, nitrogen, and chloride atoms were refined anisotropically due to the insufficient number of observations. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHEXTL 5.03 program library (Sheldrick, 1997, WI.). Crystal data are summarized in Table 1, while relevant bond distances and angles are given in Table 2.

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**Table 1. Crystal Data and Structure Analysis Results**

| | 1 | 2 |
|---|---|---|
| formula | $C_{240}H_{272}N_{16}Yb_8Cl_2Li_2O_{18}$ | $C_{58}H_{64}N_4Na_2O_4Yb$ |
| fw | 5137.84 | 1100.15 |
| space group | triclinic, $P\bar{1}$ | triclinic, $P\bar{1}$ |
| $a$ (Å) | 17.254(4) | 10.758(4) |
| $b$ (Å) | 19.145(4) | 10.987(4) |
| $c$ (Å) | 19.659(4) | 24.968(9) |
| α (deg) | 61.167(5) | 91.809(5) |
| $\beta$ (deg) | 84.757(4) | 96.237(5) |
| $\gamma$ (deg) | 74.114(4) | 116.248(5) |
| $V$ (Å$^3$) | 5465(2) | 2621(2) |
| $Z$ | 1 | 2 |
| radiation (Kα, Å) | 0.71073 | 0.71073 |
| $T$ (K) | 233 | 238 |
| $D_{calcd}$ (g cm$^{-3}$) | 1.561 | 1.394 |
| $\mu_{calcd}$ (cm$^{-1}$) | 3.476 | 1.850 |
| $F_{000}$ | 2568 | 1128 |
| $R$, $R_w$[2], GoF[a] | 0.0580, 0.1211, 1.041 | 0.0518, 0.1021, 1.055 |

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $R_w = [(\Sigma(|F_o| - |F_c|)^2/\Sigma wF_o^2)]^{1/2}$.

**Table 2. Selected Bond Distances (Å) and Angles (deg)**

| 1 | 2 |
|---|---|
| Yb(1)−Cl = 2.707(6) | Yb−N(1) = 2.401(8) |
| Yb(2)−Cl = 2.797(6) | Yb−N(2) = 2.719(8) |
| Yb(4a)-Cl = 3.066(6) | Yb−N(3) = 2.420(8) |
| Yb(1)−N(1) = 2.588(17) | Yb−N(4) = 2.693(8) |
| Yb(1)−N(2) = 2.729(16) | Yb−C(5) = 2.743(10) |
| Yb(1)−N(3) = 2.704(16) | Yb−C(6) = 2.760(9) |
| Yb(1)−N(4) = 2.535(17) | Yb−C(7) = 2.713(9) |
| Yb(1)−C(5) = 2.776(19) | Yb−C(8) = 2.695(9) |
| Yb(1)−C(7) = 2.81(2) | Na(1)−N(1) = 2.624(9) |
| Yb(1)−C(8) = 2.71(2) | Na(1)−C(1) = 2.920(12) |
| Yb(2)−N(3) = 2.579(16) | Na(1)−C(2) = 3.118(12) |
| Yb(2)−N(4) = 2.694(16) | Na(1)−C(3) = 2.869(11) |
| Yb(2)−N(5) = 2.865(16) | Na(1)−C(4) = 2.605(11) |
| Yb(2)−N(6) = 2.514(15) | Na(1)−O(1) = 2.281(9) |
| Yb(3)−N(5) = 2.455(16) | Na(1)−O(2) = 2.278(9) |
| Yb(3)−N(6) = 2.670(16) | Na(1)−N(2) = 2.460(9) |
| Yb(3)−N(7) = 2.656(15) | N(1)−Yb−N(3) = 122.5(3) |
| Yb(3)−N(8) = 2.455(16) | O(1)−Na(1)−O(2) = 90.4(4) |
| Yb(1)−Cl−Yb(2) = 86.91(16) | O(1)−Na(1)−N(2) = 101.0(3) |
| Yb(1)−Cl−Yb(4a) = 83.62(16) | O(2)−Na(1)−N(2) = 131.1(4) |
| Yb(2)−Cl−Yb(4a) = 169.8(2) | |
| N(1)−Yb(1)−N(4) = 154.9(5) | |
| N(1)−Yb(1)−Cl = 76.8(4) | |
| N(4)−Yb(1)−Cl = 78.2(4) | |
| Cl−Yb(2)−N(3) = 81.2(4) | |
| Cl−Yb(2)−N(6) = 131.7(4) | |
| N(5)−Yb(3)−N(8) = 123.2(5) | |

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**Supporting Information Available:** Listings of atomic coordinates, thermal parameters, and bond distances and angles **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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